ACTIVITY REPORT

June 2003

Natural Gas & Oil Technology Partnership

bringing department of energy national laboratories capabilities to the petroleum industry

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Note: Natural Gas and Oil Technology Partnership projects are reported according to the following schedule:

January, March, May, July, September, November	**February, April, June, August, October, December**
Drilling, Completion, and Stimulation Technology Oil and Gas Recovery Technology Diagnostic and Imaging Technology	Upstream Environmental Technology Downstream Environmental Technology Natural Gas Technology

Natural Gas and Oil Technology Partnership on the World Wide Web: http://www.sandia.gov/ngotp/

Upstream Environmental Technology

Ecological Framework to Evaluate the Effect of Size and Distribution of Releases at Upstream Petroleum Sites

(American Petroleum Institute, BP Amoco, ChevronTexaco, ExxonMobil, Gas Technology Institute, Unocal, ORNL, and LLNL)

Highlights:

- Modeling continues.
- Manuscript work continues.

Project researchers are completing the intensive modeling phase and finalizing manuscripts of the results.

Researchers developed two models that can be used to determine the threshold frequency, size and/or distribution of habitat loss resulting from exploration and production activities having a significant impact on the persistence of herbivore and/or predator populations. Models are parameterized for the Tallgrass Prairie Preserve in Osage County, OK.

Researchers are awaiting review comments for a submitted manuscript based on an earlier presentation at the American Society for Testing and Materials symposium on Landscape Ecology and Wildlife Habitat Evaluation: Critical Information for Ecological Risk Assessment, Land-Use Management Activities, and Biodiversity Enhancement Practices. The manuscript is expected to be published in a related book and was authored by ORNL and LLNL scientists: R. A. Efroymson, T. M. Carlsen, H. I. Jager, T. Kostova, E. A. Carr, W. W. Hargrove, J. Kercher, and T. L. Ashwood. The title is "Toward a Framework for Assessing Risk to Vertebrate Populations from Brine and Petroleum Spills at Exploration and Production Sites."

The ORNL manuscript submitted to Conservation Biology entitled "Simulated Effects of Habitat Loss and Fragmentation on the American Badger (*Taxidea taxus*)" was returned with recommendations to submit it to a modeling journal. The manuscript was revised and submitted to *Landscape Ecology*.

LLNL made final revisions to the paper, "Individual-Based Spatially-Explicit Model of an Herbivore and Its Resource: The Effect of Habitat Reduction and Fragmentation," which was accepted for publication in a special issue on Mathematical Population Dynamics in *Comptes Rendus d'Academy de Science: Biologie*. LLNL continued work on a second manuscript, titled "The Effect of Area Size, Predation and Fragmentation on the Time to Extinction of Prairie Vole Populations: Simulation Studies via a Trophic Individual-Based Model." This report will be submitted to *Ecological Modeling* during the next reporting period.

Estimation and Reduction of Air Quality Modeling Uncertainties

(Envair, EPRI, and LBNL)

No report received.

Remote Sensing for Environmental Baselining and Monitoring

(ChevronTexaco, UC-Davis, and ORNL)

Project inactive due to delay in 2003 funding. Funding just received at the end of the reporting period.

Modeling of Water-Soluble Organic Content of Produced Water

(ChevronTexaco, ConocoPhillips, Shell, Statoil, and ORNL)

Highlight:

- Paper prepared for submission to *Chemosphere*.

A paper was prepared for submission to *Chemosphere* on the modeling of produced water analysis results carried out between 1999 and 2002 at ORNL.

The title of the paper is "Analysis and Modeling of Hydrocarbon Contamination in Produced Water," with coauthors J. McFarlane, D.T. Bostick, H. Luo. The abstract is as follows:

Produced water remediation to National Pollution Discharge Elimination System (NPDES) target levels can represent a significant cost for oil production in the Gulf of Mexico. Off-shore analysis and remediation of produced water is expensive, and the relatively high polar content of Gulf of Mexico crude oil also means a higher solubility of organic components in the aqueous phase. In addition, neither are the identities of the water-soluble components well known, nor are their concentrations in the produced water brines. These concentrations will be affected by physical variables such as pH and temperature, but also by the depth of the formation and the age of the well. This work endeavored to address part of this gap in the knowledge base, both through characterization of simulated produced water contacted with actual crude oil samples from the Gulf of Mexico, and by modeling of the produced water/crude oil system using chemical thermodynamics. Because of the focus on semi-volatile components, the chemical system was modeled as a liquid-liquid equilibrium with activity coefficients based on a functional group analysis. A random sampling method was introduced to allow uncertainties in the input data to be reflected in the results of the computation. The model has successfully reproduced parametric studies carried out at ORNL, allowing explanation of changes in solubility observed with variations in pH and temperature.

Science-Based Methods to Assess Risks Attributable to Petroleum Residues Transferred from Soil to Vegetation

(ChevronTexaco, PERF UC-Berkeley, UC-Davis, and LBNL)

Highlights:

- Air samplers and irrigation system installed in chambers.
- Plant uptake experiment begun.

LBNL and UC-Davis researchers initiated the first plant uptake study for wheat grass. Air samplers for monitoring particle (PM10) and gas phase polycyclic aromatic hydrocarbons (PAHs) and n-alkanes in the chamber air were installed in two chambers. The first chamber contains wheat grass growing in contaminated soil and filtered air. The second chamber contains wheat grass growing in clean soil and ambient air. Background contamination levels will be monitored to evaluate the importance of soil-to-plant transfers relative to ambient contamination. An automatic irrigation system was installed in the chamber with filtered air so that the system can remain closed during the exposure event.

The extraction, cleanup and analysis approach developed earlier for quantitating the PAHs in soil and grain was adapted for the n-alkanes. After soxhlet extraction of ~ 10 g (fresh weight) of plant material or soil with dichloromethane, the extract is dried by passing through anhydrous sodium sulfate then filtered and concentrated to 1 ml. The extract is then cleaned up using size exclusion chromatography, which separates the n-alkanes from the PAHs, followed by silica gel chromatography to remove remaining polar contaminants. The final extracts containing the alkanes and PAHs are concentrated and analyzed separately using a gas chromatography-mass spectrometry (GC/MS) isotope dilution method.

Interactive Information System on Drilling Waste Management Practices (ChevronTexaco, Marathon, and ANL)

Highlights:

- Paper presented at the Exploration and Production Environmental Conference in San Antonio, TX.
- Second year funding arrived.

A paper describing the project was presented on March 11, 2003 at the Society for Petroleum Engineers (SPE)/ Environmental Protection Agency (EPA)/ Department of Energy (DOE) Exploration and Production Environmental Conference in San Antonio, TX. The presentation was well received by the audience.

Activity was limited during May and June as researchers awaited the second year funding. The funding arrived in late May.

Researchers continued to work on the state regulatory summaries and have created several new fact sheets on individual drilling waste management technologies.

Downstream Environmental Technology

A Predictive Model of Indoor Concentrations of Outdoor $PM_{2.5}$ in Homes (Aerosol Dynamics, Western States Petroleum Association, and LBNL)

No report received.

A Predictive Model of Indoor Concentrations of Outdoor Volatile Organic Compounds in Homes (American Petroleum Institute, Western States Petroleum Association, and LBNL)

No report received.

Developing Enzyme and Biomimetic Catalysts for Upgrading Heavy Crudes via Biological Hydrogenation and Hydrodesulfurization (ChevronTexaco and ORNL)

Highlight:

- Digestion products of hydrogenase enzyme were low due to the high enzyme stability.

In the previous report, a procedure for isolation of the catalytic active center by digestion at 50°C was reported. Further analysis of the digest by size exclusion chromatography revealed that although polyacrylamide gel electrophoresis (PAGE) analysis indicated significant digestion of the hydrogenase enzyme, the amount of complex produced was very low. This was because the digestion occurred upon addition of the chemical, sodium dodecyl sulfate (SDS) during PAGE analysis and not by protease action alone. The enzyme hydrogenase is therefore, quite stable in the presence of the proteases.

In previous experiments, it was observed that the SDS destroyed catalytic activity, and therefore cannot be used in the isolation procedure. Due to the low yields of the active center using the digestion procedure, alternate approaches to obtain the catalytic center are being sought. One approach is based on genetic engineering. This is a bottom-up approach consisting of modification of the hydrogenase gene to produce just the catalytic active center. This approach was suggested by Dr. Mike Adams from the University of Georgia, Athens. Another approach is to separate the two sub-units of hydrogenase enzyme and use the sub-unit containing the Ni-Fe active center by itself for hydrogen activation. This subunit, however, may not interact with sulfur substrates and may require modification with hydrophobic groups. These approaches are being discussed with the industrial participant, ChevronTexaco.

Characterization and Reaction Behavior of Sterically-Hindered Sulfur Compounds in Heavy Crudes with Nano-Sized Molybdenum Disulfide

(ChevronTexaco, BNL, and ANL)

Researchers are conducting full characterization of the synthesized materials to establish the effect of nanosizing that may lead to better hydrodesulfurization (HDS) catalysts. Since supported micro-sized cobalt molybdenum disulfide (Co-MoS_2) is the preferred HDS catalyst, researchers are synthesizing several variations of this material, with respect to Co loading to adjust the Co/Mo ratio. The plan is to establish the definite role Co plays in sulfur removal. The synthesis of three such samples is complete. These samples are presently being characterized via elemental analysis, transmission electron microscopy (TEM) and X-ray diffraction (XRD). The feedback from preliminary HDS runs conducted at ANL is serving as a guideline in the formulations of the next generation HDS catalysts.

The above-mentioned unsupported MoS_2 (0.2 g), $CoMoS_2$ (0.2 g) and MoS_2/alumina (1.0 g) catalysts, as well as the commercial $CoMoS_2$/alumina (1.0 g) used as benchmark, were retested using 1.44 weight percent dibenzothiophene (DBT) in hexadecane. The catalysts (all at 400° C, 286 psig H_2, and 17 WHSV) showed the following initial activities.

The commercial catalyst gave about 86% conversion of DBT to cyclohexylbenzene and biphenyl, with about 94% selectivity to biphenyl. Unsupported MoS_2 showed 0% conversion of DBT. Unsupported $CoMoS_2$ gave about 19% conversion of DBT with 100% selectivity to biphenyl. MoS_2/alumina gave about 40% conversion of DBT with 100% selectivity to biphenyl.

Following the initial testing with DBT feedstock, the commercial catalyst and the MoS_2/alumina were tested using a 1.64% solution of 4, 6-dimethyldibenzothiophene (DMDBT) in hexadecane, and then retested using the DBT feedstock.

The commercial catalyst gave about 55% conversion of DMDBT and a measured yield of 47% 3,3'-dimethylbiphenyl. No hydrogenated products were observed. The difference between the conversion and yield is believed to be analytical error. The MoS2/alumina gave about 20% conversion of DMDBT and a measured yield of about 30% (sic) 3,3'-dimethylbiphenyl. No hydrogenation products were observed. As with the commercial catalyst, the difference between conversion and yield is believed to be analytical error.

Upon retesting with DBT, the commercial catalyst gave results experimentally identical to the initial testing: about 91% conversion of DBT to cyclohexylbenzene and biphenyl, with about 94% selectivity to biphenyl. MoS_2/alumina gave about 35% conversion of DBT, with 100% selectivity to biphenyl.

Measurements are being made to allow calculation of conversion per exposed metal atom on each catalyst rather than gross weight of catalyst.

Development of a Solid Catalyst Alkylation Process Using Supercritical Fluid Regeneration

(Marathon-Ashland and INEEL)

No report received.

Biocatalytic Alkane Transformation for Viscosity Reduction (ChevronTexaco and LBNL)

No report received.

Secondary Organic Aerosol Research (Aerosol Dynamics, Western States Petroleum Association, and LBNL)

No report received.

Proton Exchange Reactive Membranes for Conversion of Light Alkanes to Clean Liquid Fuel (Ceramatec, Inc. and INEEL)

No report received.

Natural Gas Technology

Molecular Engineering: Next Generation of Gas Purification Technology (ChevronTexaco, Virginia Commonwealth U, and BNL)

Researchers continued the process optimization studies. In particular, the monomer recrystallizing kinetics were investigated. The imprinting process relies on the following sequence of processing steps: 1) amorphous nano-particle formation by RESS, 2) vapor-induced recrystallizing, 3) photopolymerization, and 4) vapor extraction. The naturally crystalline monomer material is formed in a metastable amorphous state by the rapid precipitation process. The amorphous particles are then recrystallized through exposure to a template vapor. However, researchers found that the particles will also recrystallize on their own even without vapor exposure, but at a much slower rate. Therefore, imprinting process is believed to depend strongly on the timing of the sequence. In particular, the time delay between steps 1 and 2 in the above sequence is expected to significantly influence the final product morphology.

Researchers investigated the influence of the DSP monomer recrystallizing time (time after development) on both imprinted and non-imprinted particles (i.e. with and without vapor treatment). Heptane was used as the template vapor. The MIP condition was 90 minutes of sorption and the polymerization conditions was10 minutes of UV polymerization under dry nitrogen. DSP monomer nano particles were developed by RESS and were polymerized the same day, one week after RESS and two weeks after RESS in presence of template as well as without vapor treatment.

As reported earlier, SAW devices coated with DSP monomer particles show significant frequency change (up to 200%) during the first two weeks, and no substantial frequency change after two weeks. Researchers attribute the observed frequency change to DSP recrystallizing and, therefore, estimate the natural (i.e. without vapor exposure) recrystallizing time is about two weeks.

Coil-Tubing-Deployed Hard Rock Thermal Spallation Drill and Cavity Maker (Nextant, NM Tech, and LANL)

Highlight:

- The second prototype burner assembly design is complete and components are being fabricated.

NM Tech completed the design of the second prototype burner assembly and the components are being fabricated at their machine shop.

The mass flow meters and controllers for the propane and air supply systems were selected and ordered. Most of the components were received and are being installed on the burner control panel.

LANL conducted a literature review of methods to model heat flow between the formation and annular flow in a drilling well. Researchers hope to develop a simple method to estimate the heat flow into and out off the rock using one of the published heat flow models. Published models reviewed to date do not appear to be easily adapted to spallation process simulation (that is, where the heat flow direction will reverse at the point that cooling water is introduced to the annulus).

LANL is investigating methods to produce a high voltage spark in a down-hole drilling environment. Piezoelectric, high voltage pulse generators, and traditional high voltage coil spark generators are being considered.

Scintillating Fiber Neutron Detectors for Well Logging (CompuLog, Precision Drilling, Technology Services Group, and PNNL)

Highlight:

- Computalog will supply MAN-A electronics for the detector bench tests.

Repeated saw failures stalled detector fabrication. A saw vendor produced excellent cuts through the PEEK (a type of plastic) and fiber. However, the cost of the replacement saw must be shared between several projects because of the high cost ($10,000). The replacement saw is expected in mid-July.

Computalog/391545 Alberta Ltd. is supplying an electronics package identical to the MAN-A telemetry package. It will accept 16 channels of TTL/CMOS signals. This minimizes electronics work at PNNL and will speed up fabrication of a down-hole system. Computalog staff are trying to locate MCNP modeling files developed for the MAN tools. These files may give a better indication of the neutron energies at the detector location and will allow for a more functional comparison between the new detector and He^3 tubes.

225° C MWD Using Silicon-On-Insulator (SOI) Electronics (Baker Oil Tools, Eagle-Picher, Honeywell SSEC, General Atomics, Noble Engineering, Quartzdyne, and SNL)

No report received.